

International Journal of Modern Physics B  
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## STOCHASTIC DESCRIPTION OF AGGLOMERATION AND GROWTH PROCESSES IN GLASSES

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Received (received date)

Revised (revised date)

We show how growth by agglomeration can be described by means of algebraic or differential equations which determine the evolution of probabilities of various local configurations. The *minimal fluctuation* condition is used to define vitrification. Our methods have been successfully used for the description of glass formation.

### 1. Introduction

In a series of papers published during the past ten years (<sup>1, 2, 3, 4</sup>), new models of growth by agglomeration of smaller units have been elaborated, and applied to many important physical systems, such as quasicrystals (<sup>5</sup>), fullerenes (<sup>6, 7</sup>), and oxide and chalcogenide glasses, (<sup>8, 9, 10, 11</sup>). Here we shall present the main ideas on which these models are based, and briefly discuss the latest developments.

In order to make our presentation concise, the example we choose is the simplest covalent network glass known to physicists, the binary chalcogenide glass  $As_xSe_{(1-x)}$ , where  $x$  is the concentration of arsenic atoms in the basic glass-former, which in this case is pure selenium. The generalization to other covalent networks, e.g.  $Ge_xSe_{(1-x)}$ , is quite straightforward. These glasses (in the form of thin and elastic foils) are used in photocopying devices.

Whether the formation of a solid network of atoms or molecules occurs in a more or less rapidly cooled liquid, or as vapor condensation on a cold support, the most important common feature of these processes is progressive agglomeration of small and mobile units (which may be just single atoms, or stable molecules, or even small clusters already present in the liquid state) into an infinite stable network, whose topology can no longer be modified unless the temperature is raised again, leading to the inverse (melting or evaporation) process.

To describe such an agglomeration with all geometrical and physical parameters, such as bond angles and lengths, and the corresponding chemical and mechanical

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energies stored in each newly formed bond, is beyond the possibilities of any reasonable model. This is why stochastic theory is an ideal tool for the description of random agglomeration and growth processes. Instead of reconstructing all local configurations, it takes into account only the *probabilities* of them being found in the network, and then the probabilities of higher order, corresponding to local correlations. This is achieved by using the *stochastic matrix* technique. A *stochastic matrix*  $\mathbf{M}$  represents an operator transforming given finite distribution of probabilities,  $[p_1, p_2, \dots, p_N]$ , into another distribution of probabilities,  $[p'_1, p'_2, \dots, p'_N]$ . It follows immediately that such a matrix must have only real non-negative entries, each column summing up to 1.

The algebraic properties of such matrices are very well known. The main feature that we shall use here is the fact that any stochastic matrix has at least one eigenvalue equal to 1. The remaining eigenvalues have their absolute values always less than 1. This means that if we continue to apply a stochastic matrix to any initial probability distribution, after some time only the distribution corresponding to the unit eigenvalue will remain, all other contributions shrinking exponentially. This enables us to find the asymptotic probability distribution.

In what follows, we identify these probability distributions with stable or meta-stable states of the system, fixing the statistics of characteristic sites in the network. Taking into account Boltzmann factors (with chemical potentials responsible for the formation of bonds), we are able to find the glass transition temperature in various compounds. In particular, one is able to predict the initial slope of the curve  $T_g(c)$ , i.e. the value of  $(dT_g/dc)_{c=0}$  (<sup>12</sup>, <sup>13</sup>).

## 2. Stochastic matrix describing cluster agglomeration

Consider a binary selenium-arsenic glass, in which selenium is the basis glass former, and arsenic is added as modifier (although its concentration can be as high as 30%). The chemical formula denoting this compound is  $As_cSe_{(1-c)}$ , where  $c$  is the  $As$  concentration. In a hot liquid, prior to solidification, the basic building blocks that agglomerate are just selenium and arsenic atoms, indicated respectively by  $(-\circ-)$  and  $(-\bullet)$ . When the temperature goes down, clusters of atoms start to appear everywhere, growing by agglomeration of new atoms on their rim. Consider a growing cluster: one can distinguish three types of situations (we shall call them “*sites*”) on the cluster’s rim. The concentration of free  $As$  atoms in the liquid will be called  $c$  and that of  $Se$ ,  $(1 - c)$ .

We should stress here that the mathematical model we propose to analyze is quite far from reality in the particular case of  $As - Se$  binary glass, as has been shown in (<sup>17</sup>), because some of the  $AS$  atoms are five-coordinated. Our model gives better predictions for the  $Ge - Se$  binary glasses. Our aim here is to expose the basic theoretical concepts rather than get very precise predictions; for this, one needs more sophisticated models, taking into account various possibilities of different agglomeration modes, e.g. ring-forming and coordination changes.

Two choices are possible for constructing the states and transition matrix (see <sup>(14)</sup>). There are three possible kinds of sites: a selenium atom with one unsaturated bond, and an As atom presenting one or two free bonds; these are indicated by  $x = \circ -$ ,  $y = \bullet$  and  $z = \bullet -$ . To each site one of the two basic cells can attach itself, reproducing one of the initial configurations, in the specific combinations shown in the next column of the Figure 1. The attachment of *one single basic cell*, or the saturation of one single bond, is a step in the evolution. In the second choice, each step is obtained by the complete saturation of all the bonds at the rim, so that only two types of sites (denoted by  $x$  and  $y$ ) are seen on cluster's rim, assuming that the growth is of dendritic type (no small rings present). It can be shown <sup>(14)</sup> that the two approaches lead to the same results, which may be considered as a proof of the ergodicity of the proposed model. We shall choose the second version of the model for the sake of simplicity. In this case, we can take into account only the  $x$  and  $y$ -type sites, because the  $z$ -type sites transform after the next agglomeration step into an  $x$  or  $y$  type site. The elementary step in the agglomeration process, described by the transition matrix, corresponds now to the complete saturation of all the available free bonds on the rim. This is represented in Figure 1 :

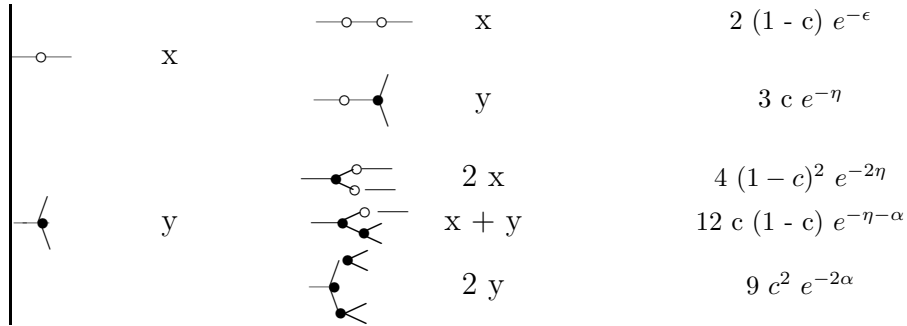


Figure 1: *States, steps and un-normalized probability factors .*

Observing that from the site  $z$  only the sites of  $x$  and  $y$  type can be produced, we can forget it and consider the dendritic growth with only two types of sites appearing all the time. Given an arbitrary initial state  $(p_x, p_y)$ , the new state results from taking into account all possible ways of saturating the bonds of the previous state's sites by the available external atoms. The un-normalized probability factors are displayed in the Figure. The non-normalized probability factors can be arranged in a matrix

$$\begin{pmatrix} 2(1-c)e^{-\epsilon} & 4(1-c)^2e^{-2\eta} \\ 8(1-c)^2e^{-2\eta} + 12c(1-c)e^{-\eta-\alpha} & 12c(1-c)e^{-\eta-\alpha} + 18c^2e^{-2\alpha} \end{pmatrix} \quad (1)$$

The normalized transition matrix is written as

$$M = \begin{pmatrix} M_{xx} & M_{xy} \\ M_{yx} & M_{yy} \end{pmatrix} = \begin{pmatrix} M_{xx} & 1 - M_{yy} \\ 1 - M_{xx} & M_{yy} \end{pmatrix} \quad (2)$$

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where the entries are obtained by normalizing the columns of the matrix (1).

$$M_{xx} = \frac{2(1-c)\xi}{2(1-c)\xi + 3c}, \quad \text{and} \quad M_{yy} = \frac{3c\mu}{2(1-c) + 3c\mu} \quad (3)$$

where we have introduced the abbreviated notation  $\xi = e^{\eta-\epsilon}$  and  $\mu = e^{\eta-\alpha}$ .

The eigenvalues of this matrix are 1 and  $M_{xx} - M_{yy} = M_{xy} - M_{yx}$ . and the stationary eigenvector is

$$\begin{pmatrix} p_x^\infty \\ p_y^\infty \end{pmatrix} = \frac{1}{M_{xy} + M_{yx}} \begin{pmatrix} M_{xy} \\ M_{yx} \end{pmatrix}, \quad (4)$$

It can be seen from Figure 1 that on the surface of an average cluster,  $p_x$  is the *Se* concentration and  $p_y$  is the *As* concentration. Now, the high homogeneity exhibited by known glass structures suggests that even in relatively small clusters, deviations from the average modifier concentration  $c$  must be negligible. Thus, *in the bulk*, the *As* concentration should be equal to  $c$ . Therefore, the condition of minimal fluctuations in the bulk concentration can be interpreted as the glass transition condition. This means that the asymptotic state is fixed by the external concentration, therefore the above eigenvector must be equal to the average distribution vector  $(1-c, c)$ . The solutions are  $c = 0$ ,  $c = 1$  and the nontrivial one

$$c = \frac{M_{yx}}{M_{xy} + M_{yx}} = \frac{6 - 4\xi}{12 - 4\xi - 9\mu}. \quad (5)$$

This equation can be checked against experiment. For example, we can evaluate the derivative  $\frac{\partial T}{\partial c} = \left(\frac{\partial c}{\partial T}\right)^{-1}$  for a given value of  $c$ . In particular, as  $c \rightarrow 0$ , we can neglect the *As-As* bond creation (equivalent to putting  $\mu = 0$  in (5)), to get

$$\left[\frac{\partial T}{\partial c}\right]_{c=0} = \frac{T_{g0}}{\ln(3/2)},$$

(where  $T_{g0}$  is the glass transition temperature of pure *Se*). This is the present-case expression of the general formula given by the stochastic approach, the fraction  $(3/2)$  being replaced by  $(m'/m)$ , where  $m$  and  $m'$  are the valences of the basic glass former and of the modifier), remaining in very good agreement with the experimental data (see <sup>15, 16, 17</sup>).

### 3. Low concentration limit.

The above scheme can be easily generalized to the case of arbitrary valence, say  $m_A$  and  $m_B$ . In that case, the stochastic  $2 \times 2$  matrix has the same form as (2), but with the entries given by

$$M_{xx} = 1 - M_{yx} = \frac{m_A(1-c)\xi}{m_A(1-c)\xi + m_Bc}, \quad M_{xy} = 1 - M_{yy} = \frac{m_A(1-c)}{m_A(1-c) + m_Bc\mu},$$

The asymptotic probability has the same form as before, as well as the zero fluctuation condition relating  $c$  with  $T$  (interpreted as the glass transition temperature). The derivative of  $c$  with respect to the temperature  $T$  gives the “magic formula”

$$\frac{dc}{dT} = \frac{1}{T} \frac{(\frac{m_A}{m_B} - \mu) \xi \ln \xi - (\frac{m_B}{m_A} - \xi) \mu \ln \mu}{[(1 - \frac{m_A}{m_B} \xi) + (1 - \frac{m_B}{m_A} \mu)]^2} \quad (6)$$

where we used the fact that  $\frac{d\xi}{dT} = -\frac{1}{T} \xi \ln \xi$ , and  $\frac{d\mu}{dT} = -\frac{1}{T} \mu \ln \mu$ . This defines the slope of the function  $T_g(c)$ , which is an important measurable quantity :

$$\frac{dT_g}{dc} = T_g \frac{[(1 - \frac{m_A}{m_B} \xi) + (1 - \frac{m_B}{m_A} \mu)]^2}{(\frac{m_A}{m_B} - \mu) \xi \ln \xi - (\frac{m_B}{m_A} - \xi) \mu \ln \mu} \quad (7)$$

The initial slope, at  $c = 0$ , is of particular interest. Its expression is very simple, taking into account that when  $c = 0$ , we have also  $\xi = \frac{m_B}{m_A}$ , which leads to

$$\left[ \frac{dT_g}{dc} \right]_{c=0} = \frac{T_{g0} (1 - \frac{m_B}{m_A} \mu)}{\ln(\frac{m_B}{m_A})} \quad (8)$$

Its value has been checked against the experiment very successfully, in more than 30 different compounds. In some cases the formula does not seem to work well; usually it comes from the change of valence of certain atoms provoked by the influence of the surrounding substrate.

One could be worried about the apparent singularity in this formula when  $m_A = m_B$ , i.e. when one deals with a mixture of two different glass formers with the same coordination number. It is not difficult to show that also in such a case a reasonable limit can be defined, as has been recently suggested by M.Micoulaut<sup>(19)</sup>. As a matter of fact, suppose that the glass transition temperature of the pure glass-former  $A$  is  $T_{g0}$ , and that of the pure glass-former  $B$  is  $T_{g1}$ . We can re-write our minimal fluctuation condition in a very symmetric manner, invariant with respect to the simultaneous substitution  $m_A \leftrightarrow m_B$ ,  $c \leftrightarrow (1 - c)$  and  $\xi \leftrightarrow \mu$  :

$$c(1 - c) [(1 - c) (1 - \frac{m_A}{m_B} \xi) - c (1 - \frac{m_B}{m_A} \mu)] = 0 \quad (9)$$

Obviously, the “pure states”  $c = 0$  or  $c = 1$  represent stationary solutions of (9) and can be factorized out. The non-trivial condition for the glass forming is thus

$$(1 - c) [1 - \frac{m_A}{m_B} \xi] - c [1 - \frac{m_B}{m_A} \mu] = 0 \quad (10)$$

Now, using the limit conditions at  $c \rightarrow 0$ ,  $T_g = T_{g0}$  and  $c \rightarrow 1$ ,  $T_g = T_{g1}$ , and introducing the generalized Boltzmann factors with the energy barriers for corresponding bond creations as  $E_{AA}$ ,  $E_{AB}$  and  $E_{BB}$ , we can write

$$E_{AB} - E_{AA} = k T_{g0} \ln(\frac{m_B}{m_A}), \quad E_{AB} - E_{BB} = k T_{g1} \ln(\frac{m_A}{m_B}), \quad (11)$$

so that the expressions  $\xi$  and  $\mu$  at the arbitrary temperature  $T$  can be written as

$$\xi(T) = e^{\frac{E_{AB} - E_{AA}}{T_{g0}} \cdot \frac{T_{g0}}{T}} = (\frac{m_B}{m_A})^{\frac{T_{g0}}{T}}; \quad \mu(T) = e^{\frac{E_{AB} - E_{BB}}{T_{g1}} \cdot \frac{T_{g1}}{T}} = (\frac{m_A}{m_B})^{\frac{T_{g1}}{T}}. \quad (12)$$

Substituting these expressions into (7) and taking the limit  $c \rightarrow 0$ , we get

$$\left. \frac{dT_g}{dc} \right|_{c=0} = \frac{T_{g0} [1 - (\frac{m_B}{m_A})^{\frac{T_{g0}-T_{g1}}{T_{g0}}}]}{\ln(\frac{m_B}{m_A})} \quad (13)$$

It is easy to see now that even when  $m_A = m_B$ , this formula has a well defined limit. Indeed, if we first set  $\frac{m_B}{m_A} = 1 + \epsilon$ , and then develop the numerator and the denominator of the above equation in powers of  $\epsilon$ , then in the limit when  $\epsilon \rightarrow 0$  we arrive at a simple linear dependence which is in agreement with common sense and with experiment as well, namely

$$\left. \frac{dT_g}{dc} \right|_{c=0} = T_{g1} - T_{g0} \quad (14)$$

This formula is also confirmed by many experiments, e.g. performed on selenium-sulfur mixtures (where  $m_A = m_B = 2$ ). The deviations from the linear law (14) observed in the *Se - Te* binary glass are explained by the fact of the chemical properties of tellurium, which changes its valence from 2 to 3 in presence of selenium.

#### 4. The effect of rapid cooling

An interesting extension of this model is obtained when we take into account the effects of rapid cooling, i.e. when the time derivative of the temperature can no longer be neglected. The treatment of this problem was suggested in <sup>(20)</sup>, and has been solved quite recently <sup>(21)</sup>.

Consider the agglomeration process defined by the above stochastic matrix,  $\vec{p}' = M\vec{p}$ , with  $\vec{p}$  representing a normalized column (a “vector”) with two entries,  $p_x$  and  $p_y = 1 - p_x$ . After one agglomeration step, representing on the average one new layer formed on the rim of a cluster, we can write

$$\Delta\vec{p} = \vec{p}' - \vec{p} = (M - \mathbf{1})\vec{p} \quad (15)$$

Let us introduce a symbolic variable  $s$  defining the progress of the agglomeration process; obviously,  $s(t)$  should be a monotonically increasing function during the glass transition. If the temperature variation is so slow that the derivative  $dT/dt = (dT/ds)(ds/dt)$  can be neglected (which is often called the *annealing* of glass), the master equation of our model can be written as

$$\Delta\vec{p} = \frac{\partial\vec{p}}{\partial s} \Delta s = (M - \mathbf{1})\vec{p} \Delta s$$

where the variation  $\Delta s$  represents one complete agglomeration step. If we want to use real time  $t$  as an independent parameter, we should write

$$\frac{d\vec{p}}{dt} = \frac{\Delta\vec{p}}{\Delta s} \frac{ds}{dt} = \tau^{-1} \frac{\Delta\vec{p}}{\Delta s} = \frac{1}{\tau} (M - \mathbf{1})\vec{p} \quad (16)$$

We have introduced here the new entity  $\tau = (ds/dt)^{-1}$  which can be interpreted as the average time needed to complete a new layer in any cluster, or alternatively, the time needed for an average bond creation. Now, if the temperature varies rapidly

enough, the matrix  $M$  can no longer be considered as constant. The equation (16) must be modified according to the well known “moving target” principle. That is, the *total* derivative of  $\vec{p}$  with respect to  $t$  should read:

$$\frac{d\vec{p}}{dt} = (M - \mathbf{1}) \frac{ds}{dt} \vec{p} + \frac{\partial M}{\partial T} \frac{dT}{dt} \vec{p} = \frac{d\vec{p}}{dt} = \left[ \frac{1}{\tau} (M - \mathbf{1}) + q \frac{\partial M}{\partial T} \right] \vec{p} \quad (17)$$

where we supposed linear dependence of the temperature on time, so that the derivative  $dT/dt$  can be denoted by constant cooling rate  $q$ . In the two-dimensional case only one component of  $\vec{p}$  is independent, because  $p_x + p_y = 1$ . Let us choose  $p_y$  (whose asymptotic value should be equal to  $c$ ) as independent variable. Then (17) will reduce to the single equation :

$$\frac{dp_y}{dt} = \frac{1}{\tau} \left[ (M_{yy} - 1) p_y + M_{yx} (1 - p_y) \right] + q \left[ \frac{\partial M_{yy}}{\partial T} p_y + \frac{\partial M_{yx}}{\partial T} (1 - p_y) \right] \quad (18)$$

where we have used the fact that  $p_x = 1 - p_y$ ,  $M_{xx} = 1 - M_{yx}$  and  $M_{yy} = 1 - M_{xy}$ .

What remains is just simple algebra. After a few operations we find the asymptotic value of  $p_y$ , denoted  $p_y^\infty$ , obtained when we set  $dp_y/dt = 0$  :

$$p_y^\infty = \frac{M_{yx} + \tau q \left( \frac{\partial M_{yx}}{\partial T} \right)}{(M_{xy} + M_{yx}) + \tau q \left( \frac{\partial (M_{xy} + M_{yx})}{\partial T} \right)} \quad (19)$$

As in the former case, we define the glass transition temperature by solving the zero-fluctuation condition  $p_y^\infty = c$ . The quasi-equilibrium condition thus obtained can be written in a form displaying an apparent symmetry between the two ingredients (“A” and “B”) of binary glass. As in the previous case (when  $q = 0$ ), the limit values  $c = 0$  and  $c = 1$  represent stationary solutions, which is obvious (no local fluctuations of concentration  $c$  are possible when there is no ingredient other than A or B atoms alone). After factorizing out  $c(1 - c)$ , we get

$$\frac{m_B}{m_A(1 - c)\xi + m_B c} - \frac{m_A}{m_A(1 - c) + m_B c\mu} = \frac{\tau q}{T} m_A m_B \left[ \frac{c\mu \ln \mu}{[m_A(1 - c) + m_B c\mu]^2} - \frac{(1 - c)\xi \ln \xi}{[m_A(1 - c)\xi + m_B c]^2} \right] \quad (20)$$

where we have used the fact that  $\frac{\partial(\ln \xi)}{\partial T} = -\frac{\ln \xi}{T}$ ,  $\frac{\partial(\ln \mu)}{\partial T} = -\frac{\ln \mu}{T}$ . The above formula seems quite cumbersome, but it become much simpler in the low concentration limit,  $c \rightarrow 0$ . Close to  $c = 0$  we get

$$\frac{m_B}{m_A} - \xi + \frac{\tau q}{T} \frac{m_B}{m_A} \ln \xi = 0 \quad (21)$$

(quite obviously, in the limit  $c \rightarrow 1$  one gets the same formula switching  $m_A$  with  $m_B$  and replacing  $\xi$  by  $\mu$ ). Replacing  $\xi$  by the expression (12), we arrive at :

$$\left[ 1 - \left( \frac{m_B}{m_A} \right)^{\frac{T_{g0} - T}{T}} \right] + \left( \frac{\tau q}{T} \right) \frac{T_{g0}}{T} \ln \left( \frac{m_B}{m_A} \right) = 0. \quad (22)$$

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It is easy to see that independently of the ratio  $m_B/m_A$ , for temperatures  $T$  above  $T_{g0}$  we must have  $q < 0$ , and vice-versa, during rapid cooling the glass transition occurs at the temperature  $T > T_{g0}$ .

The dimensionless combination  $(\tau q)/T$  defines the quenching rate as the product of  $(1/T)(dT/dt) = d(\ln T)/dt$  by the time constant  $\tau$ , characterizing the kinetics of the agglomeration process, i.e. the average time it takes to create a new bond. It may depend weakly on the temperature, but for the sake of simplicity suppose it is constant. It can be determined by comparing formula (22) with the experimental data. To take an example, let us again consider the selenium-arsenic glass at  $c \rightarrow 0$  (almost pure selenium with a small addition of As). We know that in this case  $T_g \rightarrow T_{g0} = 318^0K$ . The formula (22) then gives the quasi-linear dependence of  $\Delta T = T - T_{g0}$  on the quenching rate  $q$ : for  $T_g = 328^0K$  (i.e.  $\Delta T = 10^0K$ ) we get  $\tau q = -10.38$ ; for  $T_g = 338^0K$  (i.e.  $\Delta T = 20^0K$ ) we get  $\tau q = -21.51$ ; for  $T_g = 348^0K$  (i.e.  $\Delta T = 30^0K$ ) we get  $\tau q = -32.26$ , and so forth.

Finally, if we want to establish the formula for a pure glass-former, without any modifier, we should take the limit  $(m_A/m_B) \rightarrow 1$  and  $\mu \rightarrow \xi$ ; we then get

$$\frac{T - T_{g0}}{T} + \left(\frac{\tau q}{T}\right) \frac{T_{g0}}{T} = 0 \quad \text{or} \quad T - T_0 = \Delta T_g = -(\tau q) \frac{T_{g0}}{T}. \quad (23)$$

Eventually, the deviations from this simple dependence may indicate that the characteristic time  $\tau$  depends on  $T$ . This can shed more light on the agglomeration kinetics in various glass-forming liquids. More details can be found in <sup>(18)</sup>, <sup>(21)</sup>

### Acknowledgements

Enlightening discussions with R.Aldrovandi, R.A.Barrio and M.Micoulaut are gratefully acknowledged.

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